SPIN DIFFUSION AND SELECTIVE EXCITATION NMR TECHNIQUES FOR COAL STRUCTURE STUDIES

Naresh K. Sethi
Amoco Oil Research Department
Naperville, Illinois- 60566

ABSTRACT

The use of selective excitation NMR technique using DANTE pulse sequence is presented as a method to obtain higher resolution in the CP/MAS spectrum of coals. This technique is shown to work very well in isolating narrow individual resonance lines from otherwise broad NMR bands usually obtained for coals. Study of carbon spin diffusion is also discussed as a means of obtaining structural information on coals. The feasibility of observing carbon spin diffusion in coals with spin labelling and matching of magic angle spinning frequency with the chemical shift difference is discussed. This method is suggested as a possible means to derive aromatic-aliphatic carbon connectivity information.

INTRODUCTION

Solid state ^{13}C NMR is widely accepted as an important analytical technique for coal characterization. The extent of structural information available from solid state NMR experiments on coals is, however, limited. A typical cross-polarization/magic angle spinning (CP/MAS) spectrum of coals shows two broad lines, often without much fine structure, attributed to unsaturated and saturated carbons. It is well known that the nature of NMR line broadening in coals is mainly inhomogenous, i.e., extensive overlap of resonance lines occurs due to a distribution of slightly different carbon structure types (1). It is often desirable to determine the number of unique lines that comprise the broad band as an important step for elucidating the structural features of these materials. Due to inhomogeneous nature of line-broadening, not much gain in resolution is expected by obtaining the spectrum at higher magnetic field strength. An approach to achieving higher resolution is proposed here with the use of selective excitation pulse techniques (2). A series of experiments are performed to resolve the broad band into unique resonance lines. A set of such experiments can be used to reveal extended information previously obscured by overlap.

Another experiment which can provide useful information on coal structure is the study of carbon spin diffusion. Several studies reported previously have used carbon and proton spin diffusion under favorable circumstances to obtain information on the domain size in heterogenous solids (3), intimacy of mixing in polymer blends(4) and carbon-carbon connectivities in amino acids(5). Spin diffusion between spectrally resolved carbons (also refered to as spectral spin diffusion) is induced largely via the homonuclear dipolar coupling. The diffusion rate is thus dependent upon the internuclear distance through the strength of their dipole-dipole coupling. Observing carbon spin diffusion in coals, however, is extremely difficult due to the statistical distribution of C-12 and C-13 isotopes which renders average dipole-dipole coupling to be 10-15 Hz and thus spin diffusion rate is very slow (.1 to .01 s^{-1}). Spin diffusion rate is further reduced by magic angle spinning and coupling of carbons with the protons. Therefore, to observe carbon spin diffusion in coals very long mixing time (1-100 s) with proton decoupling field kept on is required. This places an excessive demand on the instrument performance, but more importantly the spin lattice relaxation times can compete with spin diffusion rate, making the experiment impossible. In this paper we show that it is feasible to observe carbon spin diffusion in coals by a combination of spin labelling and adjusting the rotor spinning frequency to be equal to the chemical shift difference (in Hz) of two resonance lines. This work is primarily inspired by recent articles on rotation enhanced spin diffusion in dilute spin systems by Ernst and co-workers(6) and Veeman and co-workers(7). They have shown that under the conditions of rotary resonance, spin diffusion rate can be enhanced by an order of magnitude. With this condition fullfilled spin diffusion between aromatic and aliphatic carbons in coals can be observed in as short a time as 80ms.

EXPERIMENTAL

The experiments were performed on a Chem-Magnetics M-100 spectrometer operating at carbon frequency of 25.11 MHz. Normal spectrum acquisation employed cross-polarization contact time of 1ms with magic angle spinning. The spinning rate could be monitored with a tachometer during the experiment. The spinning rates were stable within 5Hz.

Selective excitation experiment proceeds as follows: cross-polarization is used to produce transverse carbon magnetization. A non-selective 90^{o} pulse then restores the magnetization along the external magnetic field direction. DANTE (2) (delays alternating with nutation for selective excitation) pulse sequence is then used to selectively convert a single resonance line back to the transverse plane which is then detected under high power proton decoupling. DANTE pulse sequence was a series of 20 pulses of 0.3 microsec. long (corresponding to a 90^{o} degree non-selective pulse of 6.5 microsec. duration). 100 - 200 microsec. delays were inserted between the pulses to perform chemical shift selectivity. An approximate analysis indicated that 85% of the original intensity could be detected. Interference of DANTE pulse sequence with magic angle spinning did not present any severe problems.

Spin diffusion experiment employed the spin-exchange pulse sequence described in detail by Maciel and co-workers(8). High power proton decoupling was applied during the entire experiment. A sequence of spectra obtained for 2D analysis were transfered to a VAX computer. The 2D data was processed in a standard way. The results are presented as a 2D contour plot.

RESULTS AND DISCUSSION

Application of selective excitation and rotation enhanced spin diffusion are illustrated here with a sample of Ill#6 coal which has been lebelled with C-13 enriched methyl groups at various reactive sites. Figure 1A shows the CP/MAS spectra of this sample. Two intense peaks in the aliphatic region of the spectrum correspond to the enriched methyl groups. These have been labelled as $O\text{-}CH_3$ and $C\text{-}CH_3$ indicating methyl groups which are bonded to oxygen and carbon respectively. Figure 1B-G shows the application of DANTE pulse sequence in isolating unique methyl resonance lines. The spacing between the pulses in DANTE sequence was adjusted in successive experiments in small increments to cover the full chemical shift range. Peaks representing unique chemical shifts were then selected to indicate the number of distinct methyl groups comprising the broad line. With this procedure only two unique resonance lines could be identified for the $O\text{-}CH_3$ groups occuring at 55 and 57 ppm whereas seven distint peaks were isolated for the $C\text{-}CH_3$ groups ranging from 16 ppm to 33 ppm (not all peaks are shown in the figure). As an example of the resolution, notice in figure 1D that three lines which are within 5 ppm can be distinguished. Such fine structure would otherwise have been obscured by overlap.

The width of the narrow lines obtained with the use of DANTE sequence approach the values that are typicaly obtained for resolved resonance lines from a polycrystalline pure compound in a CP/MAS experiment. Line-widths of the individual lines are in the range of 1-2 ppm, which is, therefore, the limit of chemical shift resolution that can be achieved.

The ability to isolate single narrow lines affords the possibility of applying other NMR techniques to identify the chemical nature of carbons giving rise to these lines. For example, use of proton multiple pulse instead of high power decoupling during detection of single lines would result in a spectra that is indictive of the number of protons attached to the carbon (J-spectroscopy)(9). Analysis of such dipolar spectra can establish the identity of each chemical shift as from methyl, methylene, methine or quaternary carbon.

Figure 2 shows a 2D contour plot for the spin exchange experiment on the same Ill#6 coal. The purpose of the experiment depicted here was to acertain the feasibility of observing carbon spin diffusion in coals. The off-diagonal ridges in the 2D plot indicate the chemical shifts that have participated in the spin exchange process during the mixing time. For the spin exchange to occur between two carbon atoms, they must neccessrarily be in close proximity to each other. Since it was unknown prior to the experiments which pair of resonance lines would satisfy such conditions, the spinning speed was set to 2630 Hz which corresponds to the chemical shift difference (in Hz) of the highest point of the $C\text{-}CH_3$ band and the highest point of the aromatic band. This was done with the assumption that the C-13 enriched methyl groups directly attached to the aromatic ring structure would have the greatest probability of undergoing spin exchange with the aromatic carbons.

Spin diffusion is enhanced for those carbon spins whose chemical shift differences are matched by the spinning frequency(6,7). To derive structural parameters from such experiments, a series of 2D experiments would have to be performed covering full shift range of aromatic and aliphatic carbon band widths. This would be very time-consuming. Alternatively it is possible to derive the same information in less time by 1D NMR with the use of DANTE sequence as demonstrated by Ernst and co-workers(6) for pure model compound.

The study of spin diffusion is an extremely promising technique for obtaining structural information about spatial positions of carbon atoms in solids(10). In particular, rotation enhanced spin diffusion appears to be a well suited technique to study the aromatic-aliphatic carbon connectivities in coals. With an appropriate choice of mixing time, it should be possible to discriminate between pairs of carbon atoms as directly bonded or two or more bonds away, i.e., aliphatic carbons alpha to the aromatic ring versus others.

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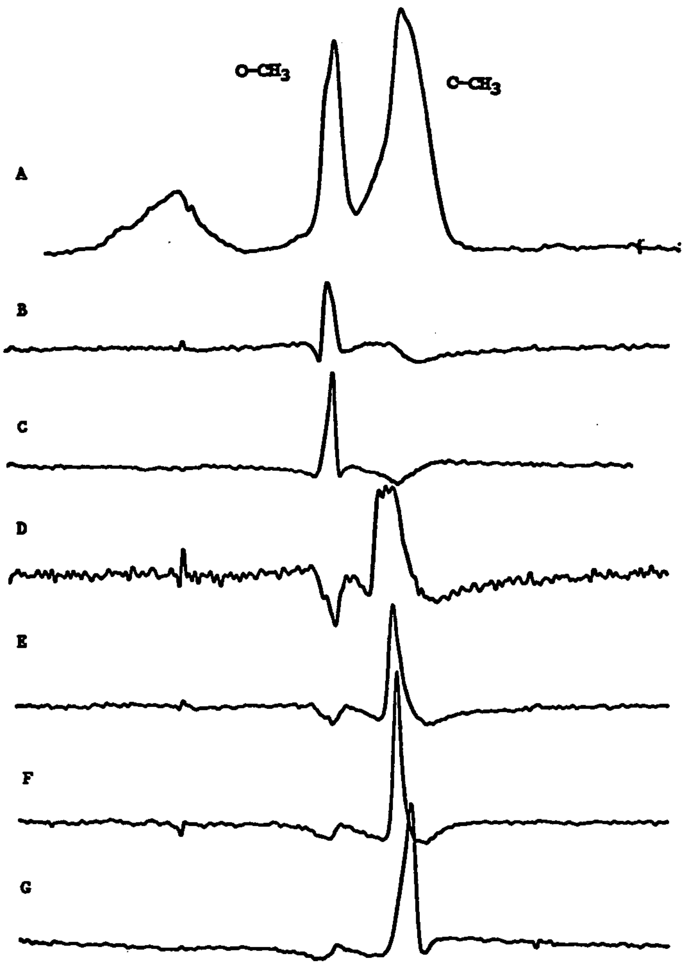

Figure 1: Application of DANTE pulse sequence to isolate invidual components of the C-13 enriched O-CH_3 and C-CH_3 groups. See text for details.

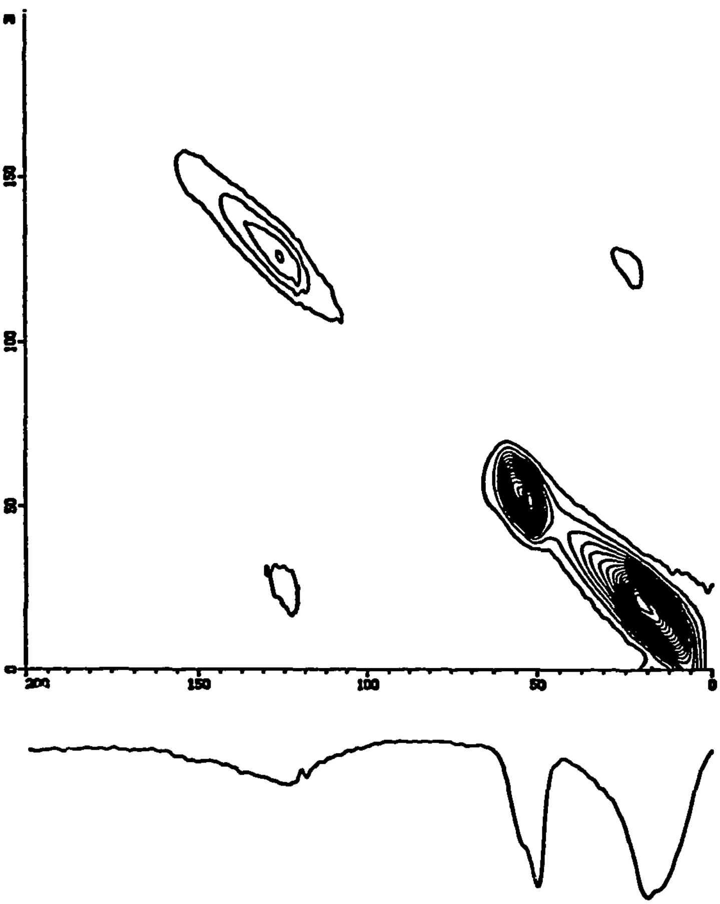

Figure 2: Absolute mode two dimensional contour plot for spin exchange with 80 ms mixing time for labelled Ill#6 coal. Spinning frequency - 2630 Hz. Markings on the axis are in ppm. See text for details.